(12) UK Patent Application (19) GB (11) 2 033 394 A

(21) Application No 7844068
(22) Date of filing 10 Nov 1978
(43) Application published 21 May 1980
(51) INT CL[3] B29C 27/08
(52) Domestic classification C3B 1D2B 1D2C 1N17 1N4H 1N6A 1N6D2 1N6D5 1N6D8 1N8A 1T1B X C3Y B500 F570 F620 G360
(56) Documents cited None
(58) Field of search C3B C3L
(71) Applicants Ciba-Geigy AG, of 4002 Basle, Switzerland
(72) Inventors Alan Robert Irvin Freestone, Graham Benson Hodgetts
(74) Agent T. Sharman

(54) Method of bonding epoxy resin

(57) Objects made of cured epoxide resin are bonded together by

a. placing the two objects in contact with each other at substantially planar mating surfaces,

b. applying a static force to the objects to urge them into intimate contact with one another at the mating surfaces

c. subjecting these surfaces to motion, relative to one another, by rotation or vibration, for a sufficient period for the frictional energy between these surfaces to heat them above the glass transition temperature(s) of the objects, and

d. stopping the relative motion whilst maintaining the static force until the mating surfaces have cooled to below the glass transition temperature(s) of the objects.

The method may be used with objects having a glass transition temperature of from about 40°C to 200°C, and provides a satisfactory bond within seconds, i.e., more rapidly than does the conventional method of applying a liquid curable adhesive composition and allowing this to cure.

Certain of the chemical formulae appearing in the printed specification were submitted in formal form after the date of filing.

GB 2 033 394 A

SPECIFICATION
Method of bonding

This invention relates to a method of bonding together two or more objects of cured epoxide resin and to articles made by this method.

Epoxide resins, by which is meant compounds containing more than one 1,2-epoxide group per average molecule, are well known materials, used for a wide variety of purposes, such as in castings and mouldings, as impregnants, and as adhesives. When two objects made of cured epoxide resin are to be bonded together, this is usually effected by applying an epoxide resin adhesive formulation to the surfaces to be joined and maintaining the objects in the requisite position whilst the adhesive cures. By using an epoxide resin adhesive the known advantages of an all epoxide resin system, such as good electrical insulation and chemical resistance, are retained and the bond has a high strength. The curing process for the adhesive is, however, often inconveniently slow, and whilst it may be accelerated by heating, this is not always convenient, due to the size or location of the objects being bonded.

There is therefore a need for a rapid method of bonding together objects made from cured epoxide resins without introducing other, epoxide-free materials. We have now found that this can be achieved by means of friction bonding under certain conditions, whereby frictional heat caused by moving one object relative to the other whilst they are held in close contact causes the epoxide resin composition in the area of contact to attain a soft, rubber-like state, this movement is then stopped, and the contacting surfaces, on cooling, form a strong bond between themselves. Full bond strength is reached in a matter of seconds, rather than of hours as is usual with a conventional epoxide resin adhesive.

This bonding technique bears a superficial similarity to friction welding, which is well known for bonding metal or thermoplastics articles. However, such materials have definite melting points and fusion occurs between the contacting surfaces. Thermoset resins, such as cured epoxide resins, on the other hand, do not melt but only soften when heated and, if heated further, they finally decompose without melting. It was therefore not to be expected that bonding of objects of cured epoxide resins could take place through the generation of frictional heat. We have further found that, provided the cured epoxide resins have a glass transition temperature within the range 40° to about 200°C, successful friction bonding can take place; cured resins having a glass transition temperature below this range can be friction-bonded, but the resultant joints are usually too weak for practical use, while resins having a glass transition temperature above this range tend to undergo, at the requisite bonding temperature, decomposition at the interface to an extent such that the joint strength is below acceptable levels.

Accordingly, this invention provides a method of joining two objects made of cured epoxide resin, the cured epoxide resin of each object having a glass transition temperature within the range 40° to 200°C, and preferably for at least one such object within the range 80° to 180°C, comprising:

a. placing the two objects in contact with each other at substantially planar mating surfaces,

b. applying a static force to the said objects to urge them into intimate contact with one another at said surfaces,

c. subjecting said surfaces to motion, relative to one another, for a sufficient period for the frictional energy between the said surfaces to heat the said surfaces to above the glass transition temperature or temperatures of the objects, and

d. stopping, or allowing to stop, the said relative motion whilst maintaining the said static force until the mating surfaces have cooled to below the glass transition temperature or temperatures of the objects.

This invention further provides articles made by this method.

By the term 'glass transition temperature', as used in this specification and claims, is meant the approximate midpoint of the temperature range over which the cured epoxide resin changes reversibly from a hard and brittle condition to a rubbery condition, as measured by differential scanning calorimetry, torsion pendulum, thermomechanical analysis, or other acceptable means.

The relative motion between the objects may be reciprocative, with one or more objects being vibrated back and forth with respect to another in the plane of the mating surfaces, or, preferably, the motion is rotational, with one or more objects being rotated against another.

When a rotational method is employed with objects held in contact end to end, the relative speeds of the surfaces in contact, and hence the frictional heating effect, reduce to zero on the axis. We have found that better results are achieved if a small area around the axis is removed from one or both mating surfaces. The area of surface removed usually represents 25% or less of the total mating surface.

The objects to be bonded will usually be rods or tubes.

The bonding of two coaxial rods end-to-end, the relative movement between them being rotational, is illustrated in Figure 1 of the accompanying drawings.

Overlap joints may be produced by rotation of a closely-fitting sleeve or ring of cured epoxide resin around cylindrical objects, also of cured epoxide resin, both of which may be stationary or one of which may be rotating relative to the other. The two rods may abut one another, or they may almost meet, and advantageously the rods are tapered towards the contiguous or adjacent faces while the sleeve or ring tapers outwards. This arrangement is illustrated in Figure 2 of the accompanying drawings.

HARDENER III
this denotes 4,4'-diaminodiphenylmethane.

HARDENER IV
this denotes phthalic anhydride.

EXAMPLE 1

Rods of circular cross section 15.7 mm in diameter were cast from Epoxide resin I and various hardeners. The nature of the hardeners, the amounts added, the curing conditions, and the glass transition temperatures (Tg) of the cured samples (measured by differential scanning calorimetry), are given in Table 1.

TABLE 1

Sample	Hardener Designation	Hardener Parts per 100 parts of Epoxide resin I	Curing conditions	Tg
A	I	25	24 hours at 20°	93°
B	II	12	24 hours at 20° and 3 hours at 70°	95°
C	II	12	24 hours at 20° and 3 hours at 95°	116°
D	II	12	3 hours at 60° and 3 hours at 95°	119°
E	III	27	16 hours at 60° and 3 hours at 95°	137°
F	III	27	16 hours at 60° and 3 hours at 95° and 3 hours at 120°	142°
G	III	27	16 hours at 60° and 3 hours at 95° and 3 hours at 120° and 3 hours at 150°	168°
H	III	27	16 hours at 60° and 3 hours at 95° and 3 hours at 120° and 3 hours at 150° and 3 hours at 180°	171°

The rod specimens were prepared by first lightly machining a flat face on one end of each rod, then counterboring these surfaces to a depth of 2 mm and a diameter of 7.5 mm. One rod was then mounted in the three-jaw self-centering chuck of a lathe and rotated at 1280 rpm. A second, similar rod was held in a chuck mounted in the tailstock of the lathe so that it could not turn but could be moved axially. This second rod was then forced against the rotating rod, pressure being applied by means of the tailstock handwheel via a calibrated compression spring device, so arranged that the axial thrust force between the two resin rods was known and reproducible. After a short period of rubbing contact between the rods as recorded in Table 2, the lathe drive was disengaged and a brake applied to bring the chuck to rest as quickly as possible, axial pressure being maintained for a further half-minute whilst the specimen cooled. The bonded specimen was then removed in one piece.

The shear strength of the bond was found by twisting one end of the article and measuring the torque on the other end at break. The results are given in Table 2, each result being the average of three replicates.

temperature or temperatures of the objects, and

d. stopping, or allowing to stop, the said relative motion whilst maintaining the said static force until the mating surfaces have cooled to below the glass transition temperature or temperatures of the objects.

2. A method according to claim 1, in which at least one cured epoxide resin has a glass transition temperature within the range 80°C to 180°C.

3. A method according to claim 1 or 2, in which the epoxide resin which is cured is a polyglycidyl ether of 2,2-bis(4-hydroxyphenyl)propane, of bis(4-hydroxyphenyl)methane, or of a novolak formed from formaldehyde and either phenol or phenol substituted in the ring by one chlorine atom or one alkyl hydrocarbon group containing from one to nine carbon atoms, and has a 1,2-epoxide content of at least 0.5 equivalent per kilogram.

4. A method according to any of claims 1 to 3, in which at least one article contains in total at most 35 parts by volume of inert filler, reinforcing material, and colouring matter per 100 parts by volume of cured epoxide resin.

5. A method according to claim 4, in which at least one article contains in total at most 20 parts by volume of inert filler, reinforcing material, and colouring matter per 100 parts by volume of cured epoxide resin.

6. A method according to claim 5, in which at least one of the articles is substantially free from inert filler, reinforcing material, and colouring matter.

7. A method according to any of claims 1 to 6, in which the motion of one object, relative to the other, is reciprocative.

8. A method according to any of claims 1 to 6, in which the motion of one object, relative to the other, is rotational.

9. A method according to claim 8, in which up to 25% of the total mating surface is removed from the area around the axis of rotation before the two objects are placed in contact with each other.

10. A method according to any of claims 1 to 9, in which bulging 'flash' in the area of the bond is removed.

11. A method according to claim 1, substantially as described herein.

12. A method according to claim 1, substantially as described herein in any of the Examples.

13. Articles made by the method of any preceding claim.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.